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(54) Polymer article and its use for controlled introduction of reagent into a fluid.

(57) A solid polymeric body comprising a polymer matrix containing a water-soluble reagent leachable into a fluid containing condensed water, said matrix being reagent permeative and insoluble in said fluid containing condensed water and the said body preferably having a softening point substantially above that of the temperature of the fluid environment in which it is to be employed is useful for the introduction of an additive reagent into said fluid particularly when said fluid is located in a subterranean formation.

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POLYMER ARTICLE AND ITS USE FOR CONTROLLED INTRODUCTION
OF AGENT INTO A FLUID.

This invention relates to a polymeric body useful for introduction of an additive into a fluid. More particularly, this invention relates to a bead containing a water-soluble additive which is leachable into a fluid containing condensed water, its method of making and the method of utilizing the bead to introduce the additive in useful amounts into the fluid.

The recovery of oil and gas from underground geological formations is of great importance in modern society, which uses vast amounts of fossil fuels for its essential energy. The individual well productivity declines over a period of time because of a number of factors, including changes in reservoir fluid characteristics, depletion of reservoir fluid characteristics, depletion of reservoir energy, decreasing permeability of the formation to the oil, the gradual dissipation of the expanding pressure transient, contamination of the well bore, reduced permeability of the oil through the region immediately surrounding the well bore and reduction of the internal diameter of the well pipe.

The response to the declining productivity was the development of numerous techniques, which has become collectively known as well workover and stimulation. The concept of fracturing or formation breakdown has been recognized to play a very important role in the application of these oil production enhancement techniques, including stimulation, acidizing, water injection and cementing of the formation.

Hydraulic fracturing has found wide usage as a well stimulation procedure for creating deep-penetrating fractures (both horizontal and vertical) that provide high capacity channels for flow from deep within the producing formation to the well as for overcoming damaged matrix permeability surrounding a wellbore. In order to produce gas or liquids from a well at a higher rate following a hydraulic fracturing treatment, the reservoir must contain enough fluids in place and the formation must not have regions of severe permeability reduction, particularly in regions adjacent to the well. Early experimental work in shallow wells demonstrated that a hydraulically formed fracture tends to heal - that is, to lose its fluid carrying capacity after the parting pressure is released -

1 unless the fracture is propped. Typical propping agents for retain-
2 ing the integrity of the fractures are nutshells, plastic beads,
3 aluminum spacers, glass beads, sand and urea prills.

4 Proppants thus provide a means for meeting the objective of
5 the fracturing which is to increase the well production by preventing
6 collapse of the formation and resultant decrease in fluid permea-
7 bility.

8 It is common practice to fracture oil wells using a water-
9 based brine fluid containing a water-soluble polymer such as hydroxy-
10 propyl guar cross-linked with a transition metal salt as is well-
11 known in the art.

12 Traditionally, the introduction of reagents downhole during
13 fracturing and other well stimulation processes is carried out by
14 forcing a solution of the reagent down the hole and into the forma-
15 tion, whereupon it becomes absorbed onto the formation and released
16 slowly from it. Unfortunately, the rate of release is variable and
17 generally is quite fast.

18 It is known to force plastic beads of ethylene-vinyl acetate
19 copolymers into the formation, but these beads are generally too
20 large to get into the fractures formed in the formation since smaller
21 beads would dissolve too rapidly. Further, the beads are too soft
22 for the proppant function.

23 When fracturing is complete and the well is put into produc-
24 tion, the flowing connate water may contain unstable salts which can
25 precipitate and form scales on the production tubing. It is possible
26 to inhibit the formation of scale by introducing a phosphonate scale
27 inhibitor continuously downhole at a level of a few parts per
28 million. It would be preferred to place the scale inhibitor downhole
29 in a solid form during the fracturing operation and allowing it to
30 leach back with the produced water; however, the scale inhibitor is
31 too quickly solubilized to have a lasting effect in the downhole
32 application.

33 It is known from British Patent Specification 1,290,554 to
34 inhibit scale formation downhole by supplying downhole a solid linear
35 carboxylic polymer having low molecular weight and in which the
36 carboxylic groups are neutralized by an alkaline earth or other
37 insolubilizing cation to an extent such that the polymer has a con-

1 trolled low solubility in water. It is stated in that specification
2 that water-soluble scale inhibitors may also be supplied downhole
3 with the substantially water insoluble polymer beads.

4 Beads containing an oil-soluble reagent having wax crystal
5 modifier activity dispersed in a polymeric matrix have been sold in
6 the United States of America and used therein for oil production from
7 an underground geological formation to inhibit the deposition of wax
8 from the oil onto the walls of structures through which the produced
9 oil was passed.

10 It is an object of this invention to provide an article and
11 its use to enhance the production of hydrocarbons from geological
12 reservoirs, more particularly from fractured formations.

13 It has been an additional object to devise a composition for
14 providing controlled release of a reagent downhole, in a pipeline, in
15 other fluids containing condensed water.

16
17 It is possible to provide for the introduction of an addi-
18 tive reagent into a fluid containing condensed water by providing
19 solid polymeric bodies, each comprising a polymeric matrix containing
20 a water soluble reagent such as a foamer, scale inhibitor, corrosion
21 inhibitor, biocide, surfactant, oxygen scavenger and mixtures
22 thereof. These bodies are, in use, positioned at a location where it
23 is desired to release the reagent into the fluid containing condensed
24 water and, upon contact with fluid in this location, release the
25 active reagent into the fluid.

26 Thus in accordance with this invention there is a disclosure
27 of a solid polymeric body comprising a solid polymer matrix con-
28 taining a water-soluble reagent leachable into a fluid containing
29 condensed water, said matrix being reagent permeative and the said
30 body preferably having a softening point substantially above that of
31 the temperature of the fluid in which it is to be employed and opti-
32 mally having a leach rate in which fifty percent of the reagent is
33 leached from the body in a time period up to 3 years by the fluid.

34 An object of this invention can be met in specific form by
35 beads comprising a solid copolymeric matrix of acrylamide and
36 methylenebis-acrylamide containing diethylene triamine pentakis
37 methylene phosphonic acid or a salt thereof and having a diameter

1 ranging from 0.2 to 1 mm. Such beads upon introduction downhole in a
2 stimulation operation are expected to inhibit scale deposition.

3 There is also provided a disclosure of a method for recover-
4 ing a fluid containing condensed water from an underground geological
5 formation comprising the steps of:

- 6 (a) depositing solid polymeric particulate bodies having a
7 reagent permeative solid polymeric matrix containing a
8 water-soluble reagent downhole in the fluid containing
9 condensed water producing region of the formation in an
10 amount sufficient to alter the reactive properties of
11 said fluids;
12 (b) flowing said fluids to the earth's surface through said
13 bodies in a contiguous manner thereby leaching said
14 reagent into said fluids; and
15 (c) recovering said fluids modified by the presence of an
16 active amount of said reagent.
17

18 Each of the solid polymeric bodies may consist solely of a
19 solid polymeric matrix containing the reagent or may contain a
20 region, generally an outer region, of polymeric material having a
21 lower rate of reagent permeation than that of the interior region and
22 substantially free of reagent. The polymer of such an outer region
23 or shell may be of the same material as the interior region matrix or
24 may be different, and will be selected having regard to the release
25 properties required from the polymeric bodies. The matrix containing
26 the reagent may be of uniform composition throughout its body or its
27 composition may vary, for instance having a different polymer compo-
28 sition in its outermost portions from its core portion. By appro-
29 priate selection of the polymeric materials for forming the bodies
30 and the distribution of reagent within the bodies, it is possible to
31 control the rate and duration of release of reagent into the fluid
32 containing condensed water while retaining the physical (structural)
33 integrity of the polymeric matrix.

34 It is this polymeric property of reagent permeativity which
35 makes possible the transfer of the water-soluble reagent from the
36 body which is insoluble in the fluid into the fluid containing con-
37 densed water that is in contact with the surface of the body. During
38 and after the leaching of the reagent from the reagent permeative

1 matrix of the body, the insoluble polymeric matrix retains its
2 structural integrity, which is in marked contrast to the approach
3 taught in Egypt. J. Pharm. Sci., 19 No. 1-4, pages 143-62, 1980 in
4 an article by A. Kassem et. al. entitled "Formulation and Evaluation
5 of Controlled Dissolution Phenobarbitone Macromolecular Products
6 Employing In Situ Suspension Polymerization With Methylmethacrylate"
7 wherein the reagent coated beads were compressed into a body which
8 upon reagent dissolution in the physiological aqueous fluids broke
9 down the body into its component beads, thus fully destroying the
10 structural integrity of the compressed body.

11 The polymeric bodies are preferably particles. The particle
12 size is generally at least 10 microns and preferably at least 50, and
13 usually at least 100 microns, since small particles can be difficult
14 to handle and to position permanently in their desired environment.
15 The particle size is generally less than 2 mm and preferable less
16 than 1 mm, since large particles also may be difficult to position in
17 their desired environment. Best results are generally obtained with
18 a particle size of from 50 microns to 1 mm. The particles may have
19 irregular shape and sizes, for instance, as a result of having been
20 made by crushing, but preferably the particles are of substantially
21 spherical or other uniform shape.

22 When being used in fracturing, the particles, preferably,
23 have a size and hardness and/or resistance to flow such that they can
24 be used in sand packing and will not be significantly degraded by the
25 sand. The particle size distribution will be selected so that a pack
26 of controlled permeability to fluid flow is formed and such that the
27 particles have a controlled leach rate as set forth earlier.

28 The reagent is water-soluble, and as such is mixed in a
29 hydrophilic polymerizable monomer such as acrylamide and its mix-
30 tures. The mixture is dispersed in a hydrophobic solvent and
31 thereafter polymerized in an invert suspension polymerization
32 process. The polymerizate is to be recovered as beads as taught
33 herein, wherein the reagent is dispersed in the polymeric matrix.
34 The softening point of the reagent should be above ambient
35 temperatures encountered in use.

36 The reagent may be any active reagent that is soluble in
37 water. The reagents are usefully selected from scale inhibitors,
38 surfactants, corrosion inhibitors, biocides, foamers, oxygen scaven-

1 gers and mixtures thereof.

2 (a) Scale Inhibitors

3 These reagents, usefully introduced in at least a scale
4 inhibiting amount to the fluid containing condensed water are repre-
5 sented by phosphonates, phosphate esters, inorganic phosphates, poly
6 (acrylic acid) and its salts as well as mixtures of these reagents.

7 1. Phosphonates include: amino tris-(methylenephosphonic
8 acid) and salts thereof such as the trisodium; ethylenediamine tetra-
9 rakis(methylenephosphonic acid) and salts thereof such as tetra-
10 potassium; diethylenetriamine pentakis(methylenephosphonic acid) and
11 salts thereof such as pentaammonium; hexamethylenediamine tetrakis-
12 (methylene phosphonic acid) and salts thereof; hydroxyethyl bis-
13 (phosphonic acid) and salts thereof such as disodium; etc. Useful
14 phosphonic acids may be derived from any other primary or secondary
15 amine, any nitrogen of which need not fully substituted with methy-
16 lene phosphonate moieties.

17 2. Phosphate esters

18 Useful esters include those such as triethanolamine tri-
19 phosphate or any hydroxyl group containing material which can be
20 converted to a phosphate ester. These may be present as either free
21 phosphoric acids or salts such as sodium, potassium or ammonium. The
22 above and similar alcohols used herein to provide the ester may be
23 oxyalkylated prior to formation of the phosphate ester in order to
24 obtain the desired hydrophobic-hydrophilic balance.

25 3. Inorganic phosphates

26 Useful phosphates include those such as orthophosphoric
27 acid, tripolyphosphoric acid and salts thereof, for example sodium,
28 potassium or ammonium salts.

29 4. Poly(acrylic acids)

30 Particularly useful is a poly(acrylic acid) having a weight
31 average molecular weight (\bar{M}_w) of from 1,000 to 5,000 and salts
32 thereof such as the sodium and ammonium salts.

33 (b) Surfactants

34 These reagents which can be introduced into a fractured
35 subterranean oil bearing formation in accordance with this invention
36 are usefully introduced to inhibit emulsification of the crude oil
37 with formation water, water flood injection water and/or water intro-
38 duced by such processes as steam stimulation.

1 1. Demulsifiers

2 These water-soluble reagents include polyoxyalkylene ether
3 and polyalkylene surfactants formed from the alkoxylation of alkyl
4 phenols, phenolic resins, alcohols, glycols, amines, organic acids,
5 carbohydrates, mercaptans, and partial esters of polybasic acids as
6 represented by an oxyalkylated phenol formaldehyde resin, ethylene
7 glycol and glycerol.

8 2. Other surfactants include:

9 a dispersant such as an ethoxylated alcohol or a mixture of
10 ethoxylated alcohols;

11 a wetting agent such as an alcohol ether sulfate alone or in
12 combination with ethoxylated alcohols;

13 a water-soluble polymer such as poly N,N-dimethylaminoethyl-
14 methacrylate methyl chloride quaternary;

15 an emulsifier such as an ethoxylated polyol or amine;

16 a detergent such as an ethoxylated polyol in combination
17 with phosphates sulfates, etc; and,

18 a lubricant such as an alcohol ether phosphate and salts
19 thereof.

20 (c) Corrosion Inhibitors

21 Useful reagents are those which have the property of
22 corrosion inhibition.

23 Typical examples of water-soluble corrosion inhibitors are
24 amines, diamines, fatty amines, polyamines, alkoxyated amines,
25 hydrogenated fatty amines, amides, fatty acid amides, imidazolines,
26 alkoxyated imidazolines and salts thereof quaternary amines and
27 quaternized imidazolines.

28 (d) Biocides

29 These have biocidal activity of the level exhibited by such
30 reagents as 2,2-dibromo-3-nitrilopro-pionamide, 2-methyl-4-isothia-
31 zolin-3-one, 5-chloro-2-methyl-4-iso-thiazolin-3-one, dithiocarba-
32 mate, aldehydes for example formaldehyde and glutaraldehyde, chlori-
33 nated phenols, methylenebisthiocyanates and guanidines.

34 (e) Foamers

35 Foamers as used herein include alcohol ether sulfates,
36 sulfonates, ethoxylated polyols, ethoxylated amines, quaternized
37 amines, amine oxides, amphotheics and mixtures of the foamers.

1 (g) Oxygen Scavengers

2 As used herein, oxygen scavengers remove trace amounts of
3 oxygen which may enter the fluid and thereby increase its corro-
4 sivity. Representative reagents are sodium bisulfite and hydrazine.

5 Polymeric Body

6 The polymeric matrix is reagent permeative and preferably
7 has a softening point as measured by a temperature-graded hot bar of
8 above 30°C and most preferably is above 60°C, often up to 120°C. The
9 combination of the reagent and the polymeric matrix must be such that
10 the reagent is releasable into surrounding fluid at the desired time
11 and rate either as a result of the fluid permeating through the
12 matrix to dissolve the reagent or as a result of the reagent per-
13 meating through the matrix to dissolve into the fluid, or both.

14 The polymer of the matrix is preferably formed mainly of
15 acrylic acid, acrylamide, or acrylonitrile or a mixture thereof and
16 minor amounts of at least one difunctional hydrophilic comonomer such
17 as methylene-bis-acrylamide. Small amounts of other hydrophilic
18 polymerizable monomers, for instance up to 40% by weight, generally
19 below 20% by weight and preferably below 10% by weight, may be
20 included provided they do not deleteriously affect the properties of
21 the polymer.

22 It is particularly preferred to include a small amount of
23 hydrophobic monomer(s) such as N,N-dibutyl acrylamide which are
24 useful in modification of the rate of reagent permeation from the
25 polymeric body when these monomers are incorporated into the monomer
26 mixture. The hydrophobic monomer tends to migrate toward the outer
27 layers of the polymerizing body due to their hydrophobic nature
28 relative to the reagents. The result is a body having a lower rate
29 of reagent permeation through its outer region than that of the
30 interior region. This approach provides a means of controlling the
31 leach rate of the reagent from the body.

32 The amount of reagent is generally at least 5% by weight of
33 the total body in order to maximize the amount of reagent introduced
34 into the desired location. It can be difficult to produce bodies
35 containing very high amounts of reagent and so the amount is gener-
36 ally not more than 50%, and usually not more than 30%, by weight of
37 the total body. The preferred reagent amount is usually 10 to 30% by
38 weight of the total body.

1 The invention has widely diverse applications since it makes
2 possible a controlled release of reagent into fluids containing
3 condensed water (such as crude oil, wet natural gas, and formation
4 water which includes both connate and injected) in a uniform manner
5 and over extended time periods. It makes possible the release of
6 certain reagents from previously non- or difficultly accessible and
7 diverse points such as in an oil bearing mineral formation one or
8 more miles underground.

9 This invention provides a method for the controlled intro-
10 duction of a reagent into an environment containing condensed water
11 which method comprises the steps of: placing solid polymeric bodies,
12 each body comprising a solid polymeric matrix insoluble in the
13 environment and containing a water-soluble reagent in said environ-
14 ment; and leaching out said reagent from said bodies at a controlled
15 and predetermined rate into the water of said environment.

16 In a preferred manner the invention provides a method pre-
17 venting scale formation in a fluid containing condensed water and
18 located in an underground geological formation which comprises:
19 determining a positive scaling tendency of the formation fluid; and,
20 thereafter depositing solid polymeric particulate bodies having a
21 reagent permeative solid polymeric matrix containing a water-soluble
22 reagent downhole in the fluid producing region of the formation in an
23 amount sufficient to alter the reactive properties of said fluids;
24 flowing said fluid to the earth's surface through said bodies in a
25 contiguous manner thereby leaching said reagent into said fluid; and,
26 recovering said fluid modified by the presence of an active amount of
27 said reagent. This preferred method is at times usefully modified by
28 the additional steps of interrupting the flow of said fluid from the
29 formation to the earth's surface, depositing said bodies by means of
30 a viscosified stimulation fluid containing at least one component
31 reactive with said reagent and thereafter resuming the flow of said
32 fluid to the earth's surface.

33 The method of making the bodies of a fluid containing con-
34 densed water-insoluble polymeric matrix containing substantially
35 water-soluble reagent involves forming a dispersion of a reagent and
36 liquid polymerizable material and polymerizing the polymerizable
37 material while maintaining the particles dispersed in the medium.
38 The polymerization results in the formation of a suspension of

1 polymer beads each containing reagent. The beads may be filtered or
2 otherwise separated from the hydrophobic medium. They may be washed
3 and dried, but for introduction by means of an aqueous fluid or into
4 an aqueous fluid the beads are best left in a damp and water-wetted
5 state.

6 In order to obtain uniform and fine distribution of the
7 reagent in the polymeric matrix, it is necessary for the reagent to
8 be monomer-soluble rather than hydrophobic medium soluble and pre-
9 ferably the reagent is in liquid form during polymerization of the
10 matrix. It could be introduced as a solution in water.

11 The following are examples of the invention.

12 EXAMPLE 1

13 Twenty grams of diethylene triamine pentakis(methylene phos-
14 phonate sodium salt are dissolved in 156 grams of a 50% aqueous
15 solution of acrylamide containing 2 grams of methylene-bis-acrylamide.

16 The resultant solution is then dispersed in 400 grams of
17 Isopar[®] M (an isoparaffinic solvent) contained in a one liter
18 enclosed vessel provided with a variable speed stirrer for controlled
19 agitation and a reflux condenser.

20 The speed of agitation is adjusted to give a stable dis-
21 persion and to this mixture is added 1 gram of azo-di-iso-butyroni-
22 trile. Suspension polymerization is allowed to continue for two hours
23 after which time the product within the vessel consists of a sus-
24 pension of aqueous polymeric gel beads in the Isopar[®] M.

25 The temperature of the vessel is slowly raised to the boil-
26 ing point of the Isopar[®] M and a water/Isopar[®] M azeotrope is
27 distilled over, condensed, split and the Isopar[®] M returned to the
28 vessel.

29 Refluxing is continued until no further water azeotropes
30 over which corresponds to the collection of 60 gram of water. The
31 product within the vessel now consists of a suspension of small
32 polymeric beads which are filtered, washed, and dried to give free
33 flowing beads containing approximately 20% of the scale inhibitor.

34 EXAMPLE 2

35 If the above process is repeated using 20 grams of scale
36 inhibitor reagent (as described), 136 grams of the 50% solution of
37 acrylamide, 2 grams of methylene bis-acrylamide and 5 grams of N,N-

1 dibutyl acrylamide, the beads are expected to have a shell containing
2 a high proportion of N,N-dibutyl acrylamide and have slower release
3 properties compared to the release properties of the beads of Example
4 1.

5 EXAMPLE 3

6 In order to produce a polymeric body according to this
7 invention containing a leachable corrosion inhibitor reagent, the
8 procedure of Example 1 is to be followed except that the active
9 phosphonate reagent is replaced with the same weight of the imada-
10 zoline quaternary salt of the equimolar reaction product of tall oil
11 fatty acid and diethylene triamine.

12 EXAMPLE 4

13 In order to produce a polymeric body according to this
14 invention containing a leachable demulsifier, the procedure of
15 Example 1 is followed except that the phosphonate is replaced with
16 the same weight of a water-soluble oxyalkylated phenol formaldehyde
17 resin of 2000 Mw.

18 EXAMPLES OF USE

19 The solid particles of the present invention can be used to
20 inhibit scale deposition by placing them downhole with the proppant
21 sand during the course of a fracturing operation. The outer shells
22 of this bead initially protect scale inhibitor from chelating the
23 metal cross-linker and thereby allowing the gelling of the fracturing
24 fluid.

25 To effect the placement of the particles of the invention
26 flow of fluids is shut in and a fracturing operation is carried out
27 as follows. A fracturing fluid is prepared by gelling a 2% solution
28 of potassium chloride with hydroxy propyl guar cross-linked with a
29 transition metal complex. As the fluid is pumped downhole, 8
30 lbs/1000 gallons of 20-40 mesh sand mixed with 5% of the beads of the
31 invention is added to serve as a proppant in the fractures formed in
32 the producing formation. Pump pressure is increased above the frac-
33 ture gradient of the rock formation and the fluid carries the prop-
34 pant mixture into the fractures. The well is then shut in for 24
35 hours to allow the guar gel to degrade to a low viscosity solution.
36 The released scale inhibitor from the bead not only prevents scale
37 formation from the produced fluids, but also chelates the remaining
38 metal cross-linkers for better cleanup of the fracturing gel. The

1 well is allowed to flow back and the fracturing fluid is recovered
2 leaving the proppant mixture of sand and polymer beads behind.

3 As the produced fluids flow through the proppant pack past
4 the beads, the scale inhibitor slowly leaches out and scale deposi-
5 tion is inhibited in the well bore and the flow lines and production
6 is maintained at a high level without scale blockage.

7 The particles of Example 1 can be used to prevent scale
8 deposition from produced fluids by placing them downhole with the
9 proppant sand during the course of a fracturing operation.

10 Connate water in a geological formation may have a tendency
11 to deposit scale comprising calcium carbonate, calcium sulphate,
12 strontium sulphate or barium sulphate or mixtures of at least two of
13 the above compounds. This scale may be formed during production of
14 the fluid due to temperature changes, pressure changes, turbulence,
15 or pH changes due to loss of dissolved gases. Scales may also be
16 formed when incompatible waters are mixed, for example, when sea
17 water is injected into the formation for the purpose of reservoir
18 pressure maintenance and comes in contact with the connate water. Water
19 incompatibility may also occur when the connate water mixes with the
20 fluids used in the stimulation operation. The likelihood of waters
21 to form scale in an environment can be determined by analysis of the
22 components in the water and is expressed as a scaling tendency. When
23 this scaling tendency is greater than unity, indicating that scale
24 formation is likely, this scale formation can be inhibited by using
25 these beads during a fracturing operation.

26 The particles of Example 1 can be used to prevent scale
27 deposition from produced fluids by placing them downhole with the
28 other solids used in gravel packing a well to prevent the production
29 of loose unconsolidated sand.

30 To effect the placement of the particles of Example 1, a
31 gravel packing operation is performed with a carrier fluid and the
32 proper mechanical equipment to place the packing solids at the speci-
33 fic producing zone. A screen or slotted liner is placed in front of
34 the packing to hold it in place, thereby, the formation in place. The
35 carrier fluid may be salt water, crude oil, diesel or acid fluids.
36 These fluids must be filtered to less than 2 microns. The viscosity
37 and density of the fluid depends on the specific well being treated.

1 An example might be to use a carrier fluid that is 2% potas-
2 sium chloride gelled with hydroxyethyl cellulose. The beads of
3 Example 1 are mixed with packing gravel and sand to make a slurry
4 containing about 20% by weight of the bead. The slurry is then
5 placed at the producing zone by using one of the accepted techniques.

6 As the produced fluid flows through the gravel pack con-
7 taining about 10% of the beads, the scale inhibitor slowly leaches
8 out and deposition is inhibited in the well bore, flowline and other
9 associated equipment.

10 The particles of Example 3 can be used to prevent corrosion
11 of the metal equipment by the produced fluids by placing the beads
12 downhole in a replaceable cartridge packed with the beads.

13 The cartridge could be designed to snap lock in the downhole
14 tubing so it can be periodically replaced when all the corrosion
15 inhibitor is leached out of the beads by the produced fluids passing
16 through the cartridge. The length of service can be controlled by
17 the leach out rate of the bead and by the size of the bead packed
18 cartridge.

19 As the produced fluid flows through the cartridge containing
20 the beads, the corrosion inhibitor slowly leaches out and inhibits
21 corrosion of well tubing or casing, flowline and associated equip-
22 ment.

23 The beads of Example 4 can be used to inhibit emulsification
24 of the crude oil formation water, water flood injection water and/or
25 water introduced by stimulation/workover processes by placing them
26 downhole with the proppant sand during the course of a fracturing
27 operation.

28 To effect the placement of the beads, a fracturing operation
29 is carried out as previously described.

30 As the produced fluid flows through the proppant pack past
31 the beads, demulsifier would slowly leach out to inhibit emulsion
32 formation during production operations.

33 As used herein % by weight is based on the total weight of
34 the body, polymer composition, water or bead, respectively.

CLAIMS

1. A solid polymeric body comprising a polymer matrix containing a water-soluble reagent leachable into a fluid containing condensed water, said matrix being reagent permeative and insoluble in said fluid containing condensed water.
2. A body according to claim 1 having a softening point substantially above that of the temperature of the environment in which it is to be employed.
3. A body according to claim 1 or 2 wherein said water-soluble reagent is removed from within said matrix to outside of said body at a leach rate in which fifty percent of the reagent is leached from the body in up to 3 years by said environment.
4. A body according to claim 1, 2, or 3 wherein said leachable water-soluble reagent is at least one of a foamer, scale inhibitor, corrosion inhibitor, biocide, surfactant, anti-oxidant, oxygen scavenger and mixtures of any one of these.
5. A leachable body according to any of claim 1-4 wherein said solid polymer matrix is a copolymer of acrylamide and methylene-bisacrylamide and said water-soluble reagent is the diethylenetriamine-pentakis-methylene phosphonic acid or salts thereof.
6. A body according to any preceding claim having a diameter ranging from 0.2 to 1mm.
7. A body according to any preceding claim having an outer region of solid polymeric material free of reagent.

8. A body according to claim 7 wherein said outer region is a solid polymer material having a lower rate of reagent permeation than that of the interior region.

9. A body according to any preceding claim wherein each particle has a size range of at least 50 microns and less than about 1 mm.

10. A body according to any preceding claim wherein the solid polymeric matrix has a softening point temperature ranging upwards from 30°C.

11. A body according to any preceding claim wherein the water-soluble reagent is 10 to 30% by weight of the total weight of the body.

12. A method for the controlled introduction of a water-soluble reagent into an environment containing condensed water, which method comprises the steps of:

- (a) placing solid polymeric bodies, each body comprising a solid polymeric matrix containing a water-soluble reagent, in said environment and said matrix being insoluble in said environment containing condensed water; and
- (b) leaching out said water-soluble reagent from said bodies at a controlled and predetermined rate into the water of said environment.

13. A method according to claim 12 wherein said environment is subterranean.

14. A method according to claim 13 wherein said

environment is a substantially hydrocarbon bearing formation.

15. A method according to claim 13 wherein said environment is a substantially water containing formation.

16. A method according to any of claims 12-15 wherein said reagent is a foamer, scale inhibitor, corrosion inhibitor, biocide, surfactant, anti-oxidant, oxygen scavenger, or a mixture of any of these.

17. A method according to any of claims 12-16 wherein the placing of said bodies is by means of a stimulation fluid.

18. A method according to claim 17 wherein said fluid is aqueous and said bodies are introduced into said fluid in a damp and water-wetted state.

19. A method according to claim 17 wherein said reagent is reactive with at least one component of said stimulation fluid whereby the reaction between said reagent and said component is prevented by said reagent's inclusion in said polymeric matrix.

20. A method according to any of claims 12-16 wherein the placing of such bodies is by means of a workover fluid.

21. A method for recovering a fluid containing condensed water from an underground geological formation comprising the steps of:

- (a) depositing solid polymeric particulate bodies having a reagent permeative solid polymeric matrix containing a water-soluble reagent downhole in the fluid producing region of the formation in an amount sufficient to alter the reactive properties of said fluid, said matrix being insoluble in the fluid containing condensed water;
- (b) flowing said fluid to the earth's surface through said bodies in a continguous manner thereby leaching said water-soluble reagent into said fluid; and
- (c) recovering said fluid modified by the presence of an active amount of said reagent.

22. A method according to claim 21 wherein said fluid is water.

23. A method according to claim 21 wherein said fluid is substantially a hydrocarbon.

24. A method according to claim 23 where said hydrocarbon is a crude oil.

25. A method according to claim 23 wherein said hydrocarbon is a gas.

26. A method of preventing scale formation in a fluid containing condensed water and located in an

underground geological formation which comprises:

- (a) determining a positive scaling tendency of the formation fluid and thereafter depositing solid polymeric particulate bodies having a reagent permeative polymeric matrix containing a water-soluble reagent downhole in the fluid producing region of the formation in an amount sufficient to alter the reactive properties of said fluids, said matrix being insoluble in the fluid containing condensed water;
- (b) flowing said fluid to the earth's surface through said bodies in a continuous manner thereby leaching said water-soluble reagent into said fluid; and,
- (c) recovering said fluid modified by the presence of an active amount of said reagent.

27. The method according to any of claims 21-26 having the additional steps of interrupting the flow of said fluid from the formation to the earth's surface, depositing said bodies by means of a viscosified stimulation fluid containing at least one component reactive with said reagent, and resuming the flow of said fluid to the Earth's surface.

28. A method according to any of claims 21-27 wherein said reagent is diethylenetriamine pentakis(methylene phosphonic acid or its salt and contained in said matrix in an amount ranging from 5 to 50 weight percent of the total weight of said body.

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